

What is claimed is:

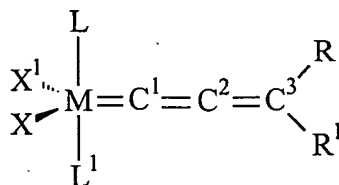
- 1 1. A catalytic complex comprising:
2 a) a metal atom selected from the group
3 consisting of ruthenium or osmium;
4 b) at least one anionic ligand ligated to said
5 metal;
6 c) at least one nucleophilic carbene ligand ligated
7 to said metal;
8 d) a further ligand ligated to said metal; and
9 e) a carbon-containing ligand ligated to said metal,
10 wherein said carbon-containing ligand is
11 selected from the group consisting of
12 alkylidene, benzylidene, indenylidene, vinylidene,
13 and allenylidene.
- 1 2. The catalytic complex of claim 1, wherein the anionic
2 ligand is selected from the group consisting of halide,
3 carboxylate, alkoxy, aryloxy, and alkyl sulfonate.
- 1 3. The catalytic complex of claim 2, wherein the anionic
2 ligand is chloride.
- 1 4. The catalytic complex of claim 1, wherein the
2 nucleophilic carbene ligand comprises a carbene carbon
3 further bonded to two heteroatoms having electronegativity
4 greater than that of carbon, wherein the heteroatoms are
5 independently selected from the group consisting of
6 nitrogen, oxygen, and sulfur.
- 1 5. The catalytic complex of claim 4, wherein the
2 nucleophilic carbene ligand comprises a substituted or
3 unsubstituted, saturated or unsaturated 1,3-diheteroatomic
4 cyclic compound.

1 6. The catalytic complex of claim 1, wherein the complex
2 is linked to a solid support by means of a link between
3 said anionic ligand and said solid support.

1 7. The catalytic complex of claim 1, wherein the complex
2 is linked to a solid support by means of a link between
3 said nucleophilic carbene and said solid support.

1 8. The catalytic complex of claim 1, wherein the carbon-
2 containing ligand selected from the group consisting of
3 alkylidene, vinylidene and allenylidene is further
4 substituted with substituents selected from the group
5 consisting of hydrogen, C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀
6 alkynyl, C₂-C₂₀ alkoxy carbonyl, aryl, C₁-C₂₀ carboxylate, C₁-
7 C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, and aryloxy,
8 optionally being substituted with C₁-C₆ alkyl, halogen, C₁-C₆
9 alkoxy, or with a phenyl group substituted with halogen, C₁-
10 C₅ alkyl or C₁-C₅ alkoxy.

1 9. A catalytic complex of the formula:



2 wherein M is Os or Ru;

3 C¹, C² and C³ are sp²-hybridized carbons, wherein
4 either or both of C¹ and C² are optionally absent;

5 R and R¹ are independently selected from the group
6 consisting of hydrogen, C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀
7 alkynyl, C₂-C₂₀ alkoxy carbonyl, aryl, C₁-C₂₀ carboxylate, C₁-
8 C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, or aryloxy,
9 each R and R¹ optionally being substituted with C₁-C₅ alkyl,
10 halogen, C₁-C₆ alkoxy, or with a phenyl group substituted
11 with halogen, C₁-C₅ alkyl or C₁-C₅ alkoxy;

13 X and X¹ are independently selected from the group
14 consisting of anionic ligands; and

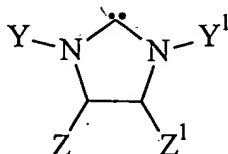
15 L and L¹ are selected from the group consisting of
16 nucleophilic carbenes, phosphine, sulfonated phosphine,
17 phosphite, phosphinite, phosphonite, ether, amine, amide,
18 sulfoxide, carbonyl, nitrosyl, pyridine and thioether,
19 wherein at least one of L or L¹ is a nucleophilic carbene.

1 ~~9.~~ The catalytic complex according to claim ~~8~~, wherein
2 only one of L or L¹ is a nucleophilic carbene.

1 ~~10.~~ A catalytic complex according to claim ~~10~~, wherein one
2 of L or L¹ is a phosphine.

1 ~~11.~~ A catalytic complex according to claim ~~9~~, wherein at
2 least 2 of X, X¹, L or L¹ are bonded together to form a
3 multidentate ligand.

1 ~~12.~~ A catalytic complex according to claim ~~9~~, wherein said
2 nucleophilic carbene is of the formula:



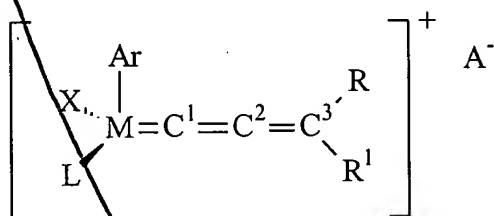
3
4 wherein

5 Y and Y¹ are independently selected from the group
6 consisting of hydrogen, C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀
7 alkynyl, C₂-C₂₀ alkoxy, carbonyl, aryl, C₁-C₂₀ carboxylate, C₁-
8 C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, or aryloxy,
9 each Y and Y¹ optionally being substituted with C₁-C₅ alkyl,
10 halogen, C₁-C₆ alkoxy, or with a phenyl group substituted
11 with halogen, C₁-C₅ alkyl or C₁-C₅ alkoxy and;

12 Z and Z¹ are independently selected from the group
13 consisting of hydrogen, C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀

14 alkynyl, C₂-C₂₀ alkoxy carbonyl, aryl, C₁-C₂₀ carboxylate, C₁-
 15 C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, or aryloxy,
 16 each Z and Z¹ optionally being substituted with C₁-C₅ alkyl,
 17 halogen, C₁-C₆ alkoxy, or with a phenyl group substituted
 18 with halogen, C₁-C₅ alkyl or C₁-C₅ alkoxy,
 19 and wherein the ring can be optionally aromatic by
 20 introduction of a further double bond in the ring.

1 ~~13~~ 14. A catalytic complex of the formula:



2
 3 wherein

4 C¹, C² and C³ are sp²-hybridized carbons, wherein
 5 either or both of C¹ and C² are optionally absent;

6 M is selected from the group consisting of Os and
 7 Ru;

8 R and R¹ are independently selected from the group
 9 consisting of hydrogen, C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀
 10 alkynyl, C₂-C₂₀ alkoxy carbonyl, aryl, C₁-C₂₀ carboxylate, C₁-
 11 C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, or aryloxy,
 12 each R and R¹ optionally being substituted with C₁-C₅ alkyl,
 13 halogen, C₁-C₆ alkoxy, or with a phenyl group substituted
 14 with halogen, C₁-C₅ alkyl or C₁-C₅ alkoxy;

15 X is an anionic ligand; and

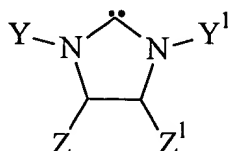
16 L is a nucleophilic carbene; and

17 Ar is an aryl substituent, bonded to M by an η⁶
 18 bond.

1 ~~13~~ 15. A catalytic complex according to claim ~~13~~ 14, wherein one
 2 of L or L¹ is a phosphine.

14
13. A catalytic complex according to claim 13, wherein at least 2 of X, Y, L or L¹ are bonded together to form a multidentate ligand.

15
14. A catalytic complex according to claim 13, wherein said nucleophilic carbene is of the formula:



wherein

Y and Y¹ are independently selected from the group consisting of hydrogen, C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₂-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, or aryloxy, each Y and Y¹ optionally being substituted with C₁-C₅ alkyl, halogen, C₁-C₆ alkoxy, or with a phenyl group substituted with halogen, C₁-C₅ alkyl or C₁-C₅ alkoxy and;

Z and Z¹ are independently selected from the group consisting of hydrogen, C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₂-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, or aryloxy, each Z and Z¹ optionally being substituted with C₁-C₅ alkyl, halogen, C₁-C₆ alkoxy, or with a phenyl group substituted with halogen, C₁-C₅ alkyl or C₁-C₅ alkoxy, and wherein the ring can be optionally aromatic by introduction of a further double bond in the ring.

15
15. A method of making a nucleophilic carbene, said method comprising:

a) contacting a substituted or unsubstituted aniline with an approximately one-half equimolar amount of paraformaldehyde under an inert atmosphere to make a first reaction mixture;

7 b) heating said first reaction mixture until said
8 paraformaldehyde dissolves;

9 c) adding an approximately one-half equimolar
10 amount of a dialkoxyacetaldehyde to make a second reaction
11 mixture; and

12 d) heating said second reaction mixture for a time
13 and under conditions sufficient to make a nucleophilic
14 carbene.

1 23. The method of claim 18, wherein said aniline is 2,4,6-
2 trimethylaniline.

1 24. The method of claim 18, wherein said aniline is 2,6-
2 diisopropylaniline.

1 25. The method of claim 18, further comprising the step of
2 hydrogenating the nucleophilic carbene to produce a non-
3 aromatic nucleophilic carbene.

1 22. A method of performing ring closing metathesis, said
2 method comprising contacting a diterminal diene with a
3 catalytic complex under conditions appropriate, and for a
4 time sufficient to produce a cyclic alkene, wherein the
5 catalytic complex comprises:

6 a) a metal atom selected from the group
7 consisting of ruthenium or osmium;

8 b) at least one anionic ligand ligated to said
9 metal;

10 c) at least one nucleophilic carbene ligand ligated
11 to said metal;

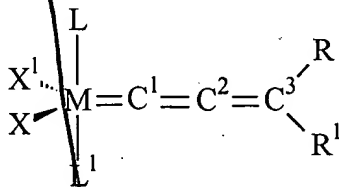
12 d) a further ligand ligated to said metal; and

13 e) a carbon-containing ligand ligated to said metal,

14 wherein said carbon-containing ligand is
15 selected from the group consisting of

16 ~~alkylidene, benzyli^Bdene, indenylidené, vinylidene,~~
17 ~~and allenylidene.~~

23. The method of claim 22, wherein the catalytic complex
has the formula:



3
4 wherein M is Os or Ru;

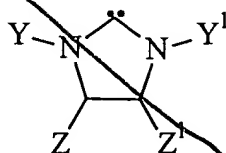
5 C¹, C² and C³ are sp²-hybridized carbons, wherein
6 either or both of C¹ and C² are optionally absent;

7 R and R¹ are independently selected from the group
8 consisting of hydrogen, C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀
9 alkynyl, C₂-C₂₀ alkoxy carbonyl, aryl, C₁-C₂₀ carboxylate, C₁-
10 C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, or aryloxy,
11 each R and R¹ optionally being substituted with C₁-C₅ alkyl,
12 halogen, C₁-C₆ alkoxy, or with a phenyl group substituted
13 with halogen, C₁-C₅ alkyl or C₁-C₅ alkoxy;

14 X and X¹ are independently selected from the group
15 consisting of anionic ligands; and

16 L and L¹ are selected from the group consisting of
17 nucleophilic carbenes, phosphine, sulfonated phosphine,
18 phosphite, phosphinite, phosphonite, ether, amine, amide,
19 sulfoxide, carbonyl, nitrosyl, pyridine and thioether,
20 wherein at least one of L or L¹ is a nucleophilic carbene.

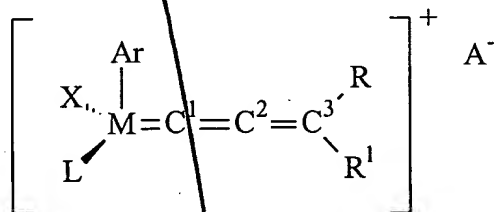
24. The method of claim 23, wherein the nucleophilic
carbene has the formula:



5 Y and Y¹ are independently selected from the group
6 consisting of hydrogen, C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀
7 alkynyl, C₂-C₂₀ alkoxy carbonyl, aryl, C₁-C₂₀ carboxylate, C₁-
8 C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, or aryloxy,
9 each Y and Y¹ optionally being substituted with C₁-C₅ alkyl,
10 halogen, C₁-C₆ alkoxy, or with a phenyl group substituted
11 with halogen, C₁-C₅ alkyl or C₁-C₅ alkoxy and;

12 Z and Z¹ are independently selected from the group
13 consisting of hydrogen, C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀
14 alkynyl, C₂-C₂₀ alkoxy carbonyl, aryl, C₁-C₂₀ carboxylate, C₁-
15 C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, or aryloxy,
16 each Z and Z¹ optionally being substituted with C₁-C₅ alkyl,
17 halogen, C₁-C₆ alkoxy, or with a phenyl group substituted
18 with halogen, C₁-C₅ alkyl or C₁-C₅ alkoxy,
19 and wherein the ring can be optionally aromatic by
20 introduction of a further double bond in the ring.

1 25. The method of claim 22, wherein the catalytic complex
2 has the formula:



4

5

7 C¹, C² and C³ are sp²-hybridized carbons, wherein
8 either or both of C¹ and C² are optionally absent;
9 M is selected from the group consisting of Os and
10 Ru;

R and R¹ are independently selected from the group consisting of hydrogen, C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₂-C₂₀ alkoxy carbonyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, or aryloxy, each R and R¹ optionally being substituted with C₁-C₅ alkyl, halogen, C₁-C₆ alkoxy, or with a phenyl group substituted with halogen, C₁-C₅ alkyl or C₁-C₅ alkoxy;

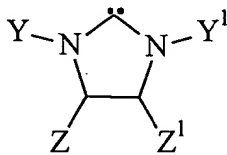
X is an anionic ligand; and

L is a nucleophilic carbene; and

Ar is an aryl substituent, bonded to M by an η^6

bond.

26. The method of claim 25, wherein the nucleophilic carbene has the formula:



wherein

Y and Y¹ are independently selected from the group consisting of hydrogen, C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₂-C₂₀ alkoxy carbonyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, or aryloxy, each Y and Y¹ optionally being substituted with C₁-C₅ alkyl, halogen, C₁-C₆ alkoxy, or with a phenyl group substituted with halogen, C₁-C₅ alkyl or C₁-C₅ alkoxy and;

Z and Z¹ are independently selected from the group consisting of hydrogen, C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₂-C₂₀ alkoxy carbonyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, or aryloxy, each Z and Z¹ optionally being substituted with C₁-C₅ alkyl, halogen, C₁-C₆ alkoxy, or with a phenyl group substituted with halogen, C₁-C₅ alkyl or C₁-C₅ alkoxy,

wherein the ring can be op
duction of a further doub

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